



Full Length Article

Auto ignition of a nitrogen-based monofuel as a function of pressure and concentration

Oren Elishav^a, Gennady E. Shter^b, Gideon S. Grader^{b,*}^aThe Nancy and Stephen Grand Technion Energy Program, Technion – Israel Institute of Technology, Haifa 3200003, Israel^bThe Wolfson Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa 3200003, Israel

HIGHLIGHTS

- The auto ignition of aqueous urea ammonium nitrate (UAN) monofuel is measured for the first time.
- The role of water in stabilizing and inhibiting the ignition is demonstrated.
- The AIT of aqueous UAN increases with pressure due to increase of water vaporization temperature.
- The boundary conditions that facilitate auto ignition of this fuel are outlined.

ARTICLE INFO

Article history:

Received 21 December 2015

Received in revised form 6 April 2016

Accepted 10 May 2016

Keywords:

Auto ignition temperature
 Chemical hydrogen storage
 Nitrogen-based alternative fuel
 Auto ignition boundaries

ABSTRACT

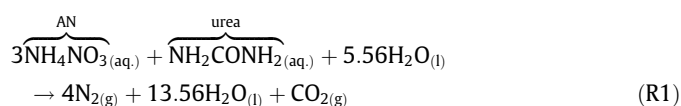
Conversion of hydrogen into a transportable and environmentally friendly chemical fuels can facilitate the implementation of renewable energy sources in our energy portfolio. In this paper we analyze a liquid mono-fuel composed of an aqueous solution of ammonium nitrate and urea (UAN), a commercial fertilizer commodity and a hydrogen carrier. In order to implement this fuel, additional information regarding its safety and combustion behavior is needed. We report on an important safety parameter of UAN, namely the auto ignition temperature (AIT). The AIT was measured in an original experimental system based on an ASTM standard under applied pressure at different water contents. The water content impacts the crystallization temperature which allows utilization of the fuel at different weather conditions. Specifically, the role of water in stabilizing and inhibiting the ignition is demonstrated, where ignition occurs in a gaseous phase after nearly complete water evaporation. Additionally, the influence of initial pressure on the ignition process was investigated. The AIT increases with pressure due to the increased water vaporization temperature. This study outlines the boundaries that support auto ignition and useful combustion of this fuel.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The enabling key to renewable energy economy hinges on the development of energy storage solutions. Once hydrogen will be produced from water economically using renewable sources, its storage and distribution on a global scale will become a major issue. While using pure hydrogen locally (i.e. refueling of cars) will be needed, large scale storage and transport of pure hydrogen requires very costly infrastructure and involves severe safety issues [1]. However hydrogen storage in the form of synthetic fuels can offer the much needed solution to this issue. Both carbon and nitrogen can serve as hydrogen carriers leading to carbon- and

nitrogen-based fuels. This paper focuses on further assessment of a nitrogen-based fuel which we have recently demonstrated as an environmentally friendly fuel that yields minimal pollutants. The fuel consists of an aqueous solution of urea and ammonium nitrate (UAN) [2] which is also used as a commercial fertilizer [3]. The ideal combustion reaction for this fuel (Reaction (R1)) produces a clean effluent gas that includes water, nitrogen and carbon dioxide.



$$\Delta\hat{H}_{\text{Rxn}}^0 = -3.34 \text{ MJ kg}^{-1}$$

* Corresponding author.

E-mail address: garder@technion.ac.il (G.S. Grader).

Previous studies characterized the decomposition of aqueous UAN at ambient pressure and under constant flow of argon and at elevated pressure [4]. At ambient pressure four endothermic stages were measured and identified. The first stage is water evaporation, followed by a second stage of urea decomposition into isocyanic acid and ammonia and the formation of biuret, the third stage is the decomposition of biuret to ammonia and isocyanic acid and finally the fourth stage is the dissociation of AN to ammonia and nitric acid. Under applied pressure the process becomes exothermic [4]. In the case of aqueous UAN the auto ignition process includes physical and chemical processes. This in turn leads to the establishment of ignitable environment that enables the combustion through radical reactions. It is quite difficult to separate and identify the individual contributions of the physical and chemical processes [5].

Aqueous UAN is a monofuel which does not need an external oxidizer, since the nitrate is the oxidizer while the ammonium and urea are the reducing agents. However, the thermal and chemical data on aqueous UAN fuel are limited. To facilitate a wide use of this fuel, practical information regarding the safety and combustion behavior is needed. Specifically, the auto ignition temperature (AIT) is an important safety parameter, defined as the minimum temperature needed for a spontaneous fuel ignition without external ignition source [6]. The AIT is not a constant value and varies with different conditions such as pressure, fuel concentration and the volume and geometry of the combustion chamber [6,7]. There are variety of methods and experimental systems that aim to measure the AIT. Because the AIT varies with the combustion parameters, to gain consistent measurements, standard methods were developed for different applications. Although there is a standard method for measuring the AIT for liquid fuel at elevated pressures, to the best of our knowledge, there is no standard method for a liquid monofuel such as aqueous UAN. Therefore, an experimental system and procedure were developed by adjusting an existing standard for liquid fuel [8].

For a given fuel there are critical conditions that sustain thermal auto-ignition, such as temperature, pressure and fuel concentration. If these critical conditions are not met, auto ignition will not occur. One of the advantages of aqueous UAN is that it is a liquid fuel. However, the dissolved AN and urea can crystallize depending on the solution concentration and temperature [9]. The effect of UAN solution composition on the properties of the fuel and thus on its usefulness in different weather conditions, has not been investigated yet. Therefore the objectives of this work were to measure the UAN fuel's AIT based on a standard setup and to investigate of the effects of applied initial pressure (up to 14 MPa) and water content (25–45%) on the auto-ignition process.

2. Experimental

The experimental system was designed based on an ASTM G72 standard for testing the autogenous ignition temperature at elevated pressure [8]. The system is composed of reaction vessel (bomb) including an inner sample holder. The vessel is prewashed and pressurized with Ultra high purity helium (99.9995%). It is heated at a constant rate in an electrical furnace controlled by a Eurotherm, (model 3216) temperature controller. A type K thermocouple is located in the middle of the furnace. The reaction vessel is positioned so that the sample is placed in the furnace hot zone. The system is equipped with a flow meter to allow a controlled gas flow during the prewashing stage (Fig. 1).

As shown in Fig. 2, the cylindrical reaction vessel (bomb) is made of stainless steel (SS) 316L having dimensions of: 62 mm OD, 23.25 mm ID and 157 mm long. The total system free volume is approximately 54 mL. The quartz liner consisting of a tube that is

closed on one end is inserted into the SS chamber to minimize possible catalytic reactions with the vessel walls. The liner dimensions are 15 mm OD and 125 mm long. A quartz tubular crucible that is 10 mm in OD and 75 mm long which contains the fuel sample, is inserted into the quartz liner. The temperature inside the vessel is measured by an inner 1.6 mm type K thermocouple that extends 15 mm into the sample crucible (Fig. 2). The pressure in the system is measured using a pressure transducer (G2, Ashcroft). Temperature and pressure signals were recorded at one second intervals. The design described above is consistent with that used in ASTM G72.

The fuel solution was prepared using AN ($\geq 99\%$, Sigma-Aldrich), urea ($\geq 99.5\%$, Sigma-Aldrich), and water (Milli-Q[®] ultra-pure water), and subsequently filtered using a 0.45 μm filter. Using volumetric pipette, 1000 mg of fuel solution was loaded to a clean and dry sample holder tube. After positioning the sample in the liner tube (see Fig. 2), the system sealed and leak tested up to 15 MPa. Before applying an initial helium pressure of 1–14 MPa, the vessel was flushed with helium in 5 cycles of pressurization and depressurization between ambient pressure and 5 MPa, followed by helium flow of 70 mL min⁻¹ for 30 min at ambient pressure.

The temperature program consisted of heating the vessel to 50 °C and soaking for 35 min at 50 °C and then increasing the temperature at a constant rate of 5 °C min⁻¹ up to 450 °C, as shown in Fig. 3a. Due to the thermal mass of the SS vessel it is difficult to maintain a constant heating rate of 5 °C min⁻¹ at the initial ramp near 50 °C. However by 70–80 °C a constant heating rate is established. Nevertheless, it is preferred to maintain at least an initial heating rate of 3 °C min⁻¹ [8]. The AIT measurement was repeated ten times at 5 MPa, yielding standard deviations of 1.4 °C and 0.24 MPa for the measured ignition temperature and pressure, respectively (Table 1S). These values were implemented to all the experiments conducted in the experimental system.

The AIT value was calculated from the time at which the second derivative of pressure with time reaches a maximum value [10] as seen by the arrow in the inset of Fig. 3b. The pressure indication point was found to be more reliable than temperature because the temperature signal is influenced by the position and size of the thermocouple as well as by the rate of heat dissipation from the system. The pressure transducer is mounted at a permanent position and is not removed during each experiment like the thermocouple.

3. Results and discussion

3.1. Auto ignition temperature

Five different aqueous UAN solutions with different water content were prepared (Table 1). The AN to Urea mass ratio was maintained at a constant value of 4:1, while the water concentration was varied from 25 wt% to 45 wt%. The above weight concentrations maintained an AN to urea stoichiometric molar ratio of 3:1 throughout all the experiments. The crystallization temperature and density of each solution are also shown in Table 1.

The AIT of each solution in Table 1 was evaluated at different initial pressures. The auto ignition was confirmed by measuring the rate pressure change (dP/dt). Based on extensive number of experiments with this system at different initial pressures and concentrations, it was concluded that auto ignition occurs at $dP/dt > 0.1 \text{ MPa s}^{-1}$ whereas slow reaction occurs at $dP/dt < 0.1 \text{ MPa s}^{-1}$. The pressure criteria refer to the maximum value for the first derivative of pressure (MPa) with time, obtained at the time of ignition (obtained from d^2P/dt^2 as explained above). It is suggested that auto ignition results from rapid reaction that

Download English Version:

<https://daneshyari.com/en/article/204963>

Download Persian Version:

<https://daneshyari.com/article/204963>

[Daneshyari.com](https://daneshyari.com)